Supporting Information for

Semivolatile organic compounds in homes: Strategies for efficient and systematic exposure measurement based on empirical and theoretical factors

Robin E. Dodson, [1*] David E. Camann,[2] Rachel Morello-Frosch,[3] Julia G. Brody,[1] Ruthann A. Rudel[1]

[1]Silent Spring Institute, 29 Crafts Street, Newton, MA USA

[2]Southwest Research Institute, 6220 Culebra Road, San Antonio, TX USA

[3] School of Public Health and Department of Environmental Science, Policy and Management, University of California--Berkeley, 130 Mulford Hall, Berkeley, CA USA

*corresponding author: dodson@silentspring.org; Tel: 617-332-4288

Contents

Details of Chemical Analysis

Sieved (<150 μm) dust samples were spiked with the required amount of surrogate solution (anthracene-d10, diazinon-d10, and p-terphenyl-d14, each at 1.0 μg) and designated samples were spiked with matrix spike solutions. Spiked samples equilibrated for 30 minutes at room temperature, then Soxhlet extracted using 6% diethyl ether in hexane for 16 hours. The extracts were concentrated to 2.5 mL or 1 mL based on the amount of dust extracted. An aliquot of 1 mL or 0.5 mL was removed for cleanup through a florisil column and the remaining extract stored as reserve. The florisil eluent was concentrated to a final volume of 1 mL or 0.5 mL with 10% ether in hexanes for analysis by GC/MS.

Analysis for the 80 neutral target analytes was performed using an Agilent 6890/5973 GC/MS in selected ion monitoring (SIM) mode. Due to the large number of target analytes, two groups of analyses were performed to minimize the number of ions in a retention time window. The first analysis was performed with a 60 m x 0.25 mm i.d. ZB-5MS column as the GC analytical column. In this analysis, a total of 52 analytes (phthalates, pesticides, PCBs and PBDEs) were the intended target analytes. The second analysis was performed with a 30 m x 0.25 mm i.d. ZB-5MS column as the GC analytical column. In this analysis, a total of 28 analytes (PAHs, sulfur PAHs, methyl phenanthrenes, chlorpyrifos, diazinon and di-n-octyl phthalate) were the intended target analytes. Since benzo(b)fluoranthene and benzo(j)fluoranthene co-eluted, the combined peak was reported as benzo(b)&(j)fluoranthene. All three surrogates were reported using the second analytical run. The GC/MS instrument was scanned to monitor 2 to 4 selected ions per analyte. Quantification was performed using isotopically labeled PAHs or pesticides as internal standards. The percent relative standard deviation (%RSD) of most of the analytes was maintained within 30% during the initial six-point standard calibration. However, several compounds in most sequences had %RSDs greater than 30%. A continuing calibration standard was processed at the beginning and end of each sequence of 15 samples. The percent difference of each analyte in the mid-level standard was generally maintained within 40% of the initial calibration value during continuing calibrations.

Quality Assurance/Quality Control (QA/QC) Methods and Results

Extensive QA/QC measures were conducted to ensure accuracy and reliability of measurements. To evaluate contamination from the laboratory, we analyzed three solvent blanks. To estimate precision, we split three samples and analyzed them as duplicates. Matrix spikes (n=3) and surrogate recoveries were used to characterize accuracy, recovery from the matrix, and extraction efficiency.

For each analyte, the method reporting limit (MRL) was defined as the maximum of the analytical detection limit and the 90^{th} percentile of the solvent blanks. MRLs were calculated on a mass-basis and converted to a concentration by dividing by the median sample mass (0.5 grams). Estimated concentrations falling above the analytical detection limit and below the MRL were flagged and were not accounted as detects when calculating %> MRL, but were used in statistical testing and graphical presentation of the concentration distributions.

Solvent blanks were used to evaluate contamination from the laboratory (Table S1). The target compounds benzyl butyl phthalate, bis(2-ethylhexyl) phthalate, bis(2-ethylhexyl) adipate, di-n-butyl phthalate, di-iso-butyl phthalate, diethyl phthalate, PBDE 47, PBDE 99, and phenanthrene were detected in at least one solvent blank. Levels were generally low (<30% minimum reported value for 5 compounds). If reported sample mass values overlapped with range of solvent blank

mass, samples were flagged as "estimated" according to our MRL determination above. To correct for potential bias in the reported levels, six compounds (benzyl butyl phthalate, bis(2-ethylhexyl) phthalate, di-n-butyl phthalate, di-iso-butyl phthalate, diethyl phthalate, and phenanthreene) were subject to blank correction by subtracting the median blank concentration. Median blank concentrations were calculated by substituting one-half the detection limit for nondetects.

Precision was evaluated using three duplicate samples. For values below the MRL, the sample-specific MRL (mass adjusted) was used in the percent difference calculations. Percent differences were typically less than 30%. For a few compounds, the average percent differences were higher than 30% (fluorene, 32%; pyrene, 34%; 2-methyl-dibenzothiophene, 39%; benz(a)anthracene, 43%; 3,6,-dimethyl phenanthrene, 43%; diethyl phthalate, 59%; anthracene, 124%; and diazinon, 130%). When only values above the MRL are included in the percent difference calculation, the average percent difference are reduced for anthracene (6%) and diazinon (50%).

Accuracy was evaluated using three matrix spike samples (Table S1). Average recoveries were mostly within 50-150% acceptance range. Benzyl butyl phthalate (200%), bis(2-ethylhexyl) phtlalate (330%), and PBDE 99 (153%), had average recoveries above 150%, although individual recoveries varied above and below 100% for these compounds and some calculated recoveries were imprecise and inaccurate because the spiked concentration was substantially lower than the concentration present in the dust. Because average recoveries were not unidirectional (systematically high), compounds were not excluded based on these recoveries.

Surrogate recoveries for all field samples were within the 50-150% acceptance range (Figure S1). Three surrogates were used: diazinon-d10, anthracene-d10, and p-terphenyl-d14. The average percent recovery for diazinon-d10 was 84%, anthracene-d10 was 96%, and p-terphenyl-d14 was 82%.

Exposure Modeling

We estimated the relative importance of dust exposure versus other household exposure pathways by calculating exposure rates (ng/day) for dust ingestion, dermal exposure through dust adherence, and inhalation of indoor air.

We estimated dust ingestion from indoor sources using the following equation:

$$Ingestion_{dust}(ng/d) = C_{dust}(ng/g) \times IR(g/d) \times AF_{GI}$$

where, C_{dust} is dust concentration (measured, ng/g), IR is dust ingestion rate (assumed 0.064 g/day), and AF_{GI} is gastrointestinal absorption fraction (assumed 0.9).

We estimated dermal exposure through dust adherence using the following equation:

$$Dermal\ Absorption_{dust}(ng/d) = C_{dust}(ng/g) \times DL(g/m^2) \times TC(m^2/hr) \times AF_{dermal} \times 24(hr/d)$$

where, C_{dust} is dust concentration (measured, ng/g), DL is dermal loading of dust (assumed 3.55 g/m^2), TC is dermal transfer coefficient (assumed 0.06 m^2/hr), and AF_{dermal} is dermal absorption fraction (assumed 0.05).

We estimated inhalation via indoor air using the following equation:

$$Inhalation_{air}(ng/d) = C_{air}(ng/m^3) \times InhR(m^3/d) \times AF_{air}$$

where, C_{air} is total air concentration (measured, ng/m^3), *InhR* is inhalation rate (assumed 14.9 m^3/d), and AF_{air} is absorption fraction for air (assumed 0.5). All exposure estimates were made over a 70 year age range and rely on exposure assumptions from Egeghy et al. 2011 and U.S. EPA 2011.

Table S1. Solvent blanks and matrix spikes for dust samples

Compound	Solvent Method Blanks (ng/g) Det. Limit	Sample #1	Sample #2	Sample #3	Matrix Spikes (%) Recovery #1	Recovery #2	Recovery #3
			Phthalates				
benzyl butyl phthalate	62.5	251	102	66.2	79	404	123
bis(2-ethylhexyl) adipate	20.8	ND	48	25.2	83	112	80
bis(2-ethylhexyl) phthalate	62.5	875	634	463	316	590	87
di-n-butyl phthalate	62.5	778	190	87.6	78	108	106
di-n-hexyl phthalate	20.8	ND	ND	ND	86	107	97
di-n-octyl phthalate	20.8	ND	ND	ND	52	62	81
di-n-pentyl phthalate	20.8	ND	ND	ND	84	107	102
di-n-propyl phthalate	29.5	ND	ND	ND	80	111	111
dicyclohexyl phthalate	20.8	ND	ND	ND	85	112	104
diethyl phthalate	62.5	525	133	438	76	94	109
diisobutyl phthalate	62.5	174	46.6	34.4	81	107	104
			Flame Retardants				
PBDE 47	20.8	ND	ND	9.51	67	237	70
PBDE 99	20.8	ND	ND	9.16	60	288	112
PBDE 100	20.8	ND	ND	ND	61	144	69
tris(2,3-dibromopropyl) phosphate	6.25	ND	ND	ND	NA	NA	NA
			Polychlorinated Biphenyls				
PCB 52	8.33	ND	ND	ND	48	62	81
PCB 105	8.33	ND	ND	ND	64	86	75
PCB 153	8.33	ND	ND	ND	70	88	73
			Polycyclic Aromatic Hydrocarbons				
acenaphthene	8.33	ND	ND	ND	70	104	73
acenaphthylene	8.33	ND	ND	ND	68	98	75
anthracene	8.33	ND	ND	ND	83	117	78
benzo(a)anthracene	8.33	ND	ND	ND	89	131	79
benzo(a)pyrene	8.33	ND	ND	ND	47	60	87
benzo(b&j)fluoranthene	16.7	ND	ND	ND	44	55	85
benzo(k)fluoranthene	8.33	ND	ND	ND	48	59	107
benzothiophene	16.8	ND	ND	ND	39	84	68
chrysene/iso-chrysene	8.33	ND	ND	ND	74	104	83
dibenz(a,e)pyrene	8.33	ND	ND	ND	57	66	101
dibenz(a,h)anthracene	8.33	ND	ND	ND	54	66	90
3,6-dimethyl phenanthrene	8.33	ND	ND	ND	89	129	69
fluoranthene	8.33	ND	ND	ND	73	114	84
fluorene	8.33	ND	ND	ND	79	112	76
indeno(1,2,3-cd)pyrene	8.33	ND	ND	ND	53	65	94
1-nitropyrene	21.7	ND	ND	ND	91	142	132

Compound	Det. Limit	Solvent Method Blanks (ng/g) Sample #1	Sample #2	Sample #3	Matrix Spikes (%) Recovery #1	Recovery #2	Recovery #3
phenanthrene	8.33	14.6	5.11	9.19	80	110	82
pyrene	8.33	ND	ND	ND	77	120	83
dibenzothiophene	16.7	ND	ND	ND	83	114	77
4,6-dimethyl dibenzothiophene	20.2	ND	ND	ND	78	109	63
2-methyl dibenzothiophene	16.6	ND	ND	ND	84	117	71
1-methyl phenanthrene	8.33	ND	ND	ND	85	117	75
2-methyl phenanthrene	8.33	ND	ND	ND	85	118	75
3-methyl phenanthrene	8.33	ND	ND	ND	86	121	75
9-methyl phenanthrene	8.33	ND	ND	ND	88	121	77
		Pesticides					
alachlor	20.8	ND	ND	ND	64	81	111
aldrin	20.8	ND	ND	ND	65	85	82
atrazine	8.33	ND	ND	ND	77	96	95
bendiocarb	58.3	ND	ND	ND	88	128	72
carbaryl	20.8	ND	ND	ND	36	89	36
carbofuran	20.8	ND	ND	ND	65	99	53
alpha-chlordane	8.33	ND	ND	ND	64	85	80
gamma-chlordane	8.33	ND	ND	ND	65	86	80
chlorothalonil	12.5	ND	ND	ND	113	83	239
chlorpyrifos	8.33	ND	ND	ND	81	110	77
cyanazine	29.2	ND	ND	ND	55	78	26
cypermethrin	66.7	ND	ND	ND	94	163	99
4,4'-DDD	8.33	ND	ND	ND	57	82	78
4,4'-DDE	8.33	ND	ND	ND	62	84	80
4,4'-DDT	8.33	ND	ND	ND	74	140	80
diazinon	8.33	ND	ND	ND	83	109	84
dicofol	20	ND	ND	ND	70	91	98
dieldrin	20.8	ND	ND	ND	68	88	84
endrin	20.8	ND	ND	ND	76	100	87
ethyl parathion	50	ND	ND	ND	80	111	95
heptachlor	8.33	ND	ND	ND	70	95	83
lindane	20.8	ND	ND	ND	65	84	79
malathion	8.33	ND	ND	ND	74	71	90
methoxychlor	20.8	ND	ND	ND	103	143	90
methyl parathion	20.8	ND	ND	ND	73	103	82
metolachlor	20.8	ND	ND	ND	65	85	115
nitrofen	20.8	ND	ND	ND	84	118	129
cis-permethrin	8.75	ND	ND	ND	77	204	78
trans-permethrin	16.7	ND	ND	ND	83	178	86
piperonyl butoxide	8.69	ND	ND	ND	81	108	117

	Solvent Method Blanks (ng/g)				Matrix Spikes (%)		
Compound	Det. Limit	Sample #1	Sample #2	Sample #3	Recovery #1	Recovery #2	Recovery #3
o-phenyl phenol	8.92	ND	ND	ND	67	93	116
prometon	20.8	ND	ND	ND	44	98	36
propoxur	41.7	ND	ND	ND	69	99	60
simazine	20.8	ND	ND	ND	74	91	118
trifluralin	12.5	ND	ND	ND	68	115	85
4-nitrotoluene	21	ND	ND	ND	47	82	71

ND = not detected

Table S2. Molecular weights and octanol-air partitioning coefficients

Compound	Abbrev.	MW[a]	log K_{oa}[b]
Phthalates			
benzyl butyl phthalate	BBP	312	9.018
bis(2-ethylhexyl) adipate	DEHA	371	12.871
bis(2-ethylhexyl) phthalate	DEHP	391	12.557
di-n-butyl phthalate	DBP	278	8.631
di-n-hexyl phthalate	DHP	334	9.799
di-n-octyl phthalate	DOP	391	12.079
di-n-pentyl phthalate	DPeP	306	9.674
di-n-propyl phthalate	DPP	250	8.053
dicyclohexyl phthalate	DCP	330	11.588
diethyl phthalate	DEP	222	7.023
diisobutyl phthalate	DIBP	278	8.412
Flame Retardants			
PBDE 47	PBDE47	486	10.686
PBDE 99	PBDE99	565	11.157
PBDE 100	PBDE100	565	11.977
tris(2,3-dibromopropyl) phosphate	TrisBP	698	7.34
Polychlorinated Biphenyls			
PCB 52	PCB52	292	8.177
PCB 105	PCB105	326	8.727
PCB 153	PCB153	361	10.777
Polycyclic Aromatic Hydrocarbons			
acenaphthene	AcNThe	154	6.044
acenaphthylene	AcNThy	152	6.272
anthracene	Anth	178	7.093
benz(a)anthracene	BaA	228	9.069
benzo(a)pyrene	BaP	252	10.859
benzo(b&j)fluoranthene	BbjFluAn	252	10.4705
benzo(k)fluoranthene	BkFluAn	252	10.732
benzothiophene	BThPhe	134	5.052
chrysene/iso-chrysene	Chrys	228	9.48
dibenz(a,e)pyrene	DBaePyr	302	13.2
dibenz(a,h)anthracene	DBahA	278	11.779
3,6-dimethyl phenanthrene	DMPhenan	206	8.033
fluoranthene	FluAn	202	8.601
fluorene	Flu	166	6.585
indeno(1,2,3-cd)pyrene	IcdPyr	276	11.547
1-nitropyrene	1NPyr	247	10.934
phenanthrene	Phenan	178	7.222
pyrene	Pyr	202	8.193
dibenzothiophene	DBTPhe	184	7.24
4,6-dimethyl dibenzothiophene	DMDBTPhe	212	8.655
2-methyl dibenzothiophene	2MDBTPhe	198	7.61
1-methyl phenanthrene	1MPhenan	192	7.776

Compound	Abbrev.	MW[a]	log K_{oa}[b]
2-methyl phenanthrene	2MPhenan	192	7.495
3-methyl phenanthrene	3MPhenan	192	7.495
9-methyl phenanthrene	9MPhenan	192	7.525
Pesticides			
alachlor	Alach	270	9.988
aldrin	Aldr	365	9.245
atrazine	Atraz	216	9.626
bendiocarb	Bendio	223	7.497
carbaryl	Carb	201	9.234
carbofuran	Crbfur	221	9.218
alpha-chlordane	aChlor	410	8.922
gamma-chlordane	gchlor	410	9.542
chlorothalonil	Chorth	266	7.137
chlorpyrifos	ChlPy	351	8.882
cyanazine	Cyan	241	12.199
cypermethrin	Cyper	416	10.825
4,4'-DDD	DDD	320	9.589
4,4'-DDE	DDE	318	9.279
4,4'-DDT	DDT	354	10.378
diazinon	Diaz	304	9.145
dicofol	Dico	370	10.025
dieldrin	Dield	381	8.588
endrin	Endr	381	8.588
ethyl parathion	Parath	291	8.744
heptachlor	Hept	373	8.02
lindane	Lind	291	7.817
malathion	Malth	330	9.059
methoxychlor	MX	346	10.161
methyl parathion	MePthion	263	8.248
metolachlor	Metol	284	9.334
nitrofen	Nitrof	284	9.622
cis-permethrin	cPerm	391	10.617
trans-permethrin	tPerm	391	10.617
piperonyl butoxide	PipBO	338	13.19
o-phenyl phenol	oPPh	170	7.457
prometon	Prom	225	10.42
propoxur	PrPx	209	8.753
simazine	Simz	202	9.594
trifluralin	Trifl	335	7.716
4-nitrotoluene	4NT	137	6.008

[a] MW = molecular weight (g/mol); obtained from EPI Suite

[b] log K_{oa} = octanol-air partitioning coefficient; estimated values obtained from KOAWIN in EPI Suite

Table S3. Measured $PM_{2.5}$ and predicted PM_6 concentrations in homes in the California Household Exposure Study

Measured $PM_{2.5}$ Concentration (μg/m3)	Predicted PM_6 Concentration (μg/m3)[a]
2.74	3.79
4.22	5.56
4.63	6.04
4.86	6.3
5.1	6.58
5.11	6.59
5.29	6.8
6.1	7.71
6.24	7.87
6.88	8.59
7.31	9.06
7.36	9.12
7.5	9.27
7.77	9.57
8.26	10.1
8.54	10.4
9.14	11.1
9.63	11.6
9.63	11.6
9.71	11.7
9.99	12
9.99	12
10.3	12.3
10.6	12.6
11.4	13.5
11.5	13.6
11.5	13.6
11.6	13.7
11.8	13.9
12.1	14.2
12.4	14.5
13.5	15.6
14.5	16.7
15.3	17.5
15.8	18
15.9	18.1
16.7	18.9
17.1	19.3
17.9	20.1

Measured $PM_{2.5}$ Concentration (μg/m3)	Predicted PM_6 Concentration (μg/m3)[a]
18.5	20.7
19.8	22
27.6	29.5
NA	12[b]
NA	12
NA	12
NA	12
NA	12
NA	12
NA	12
NA	12

[a]Predicted PM_6 concentration using linear regression model ($\log(PM_6)=0.43+0.891(\log(PM_{2.5}))$ developed from data in Long et al. 2000

[b]$PM_{2.5}$ concentration not available so assumed average predicted PM_6 concentration

NA = not available

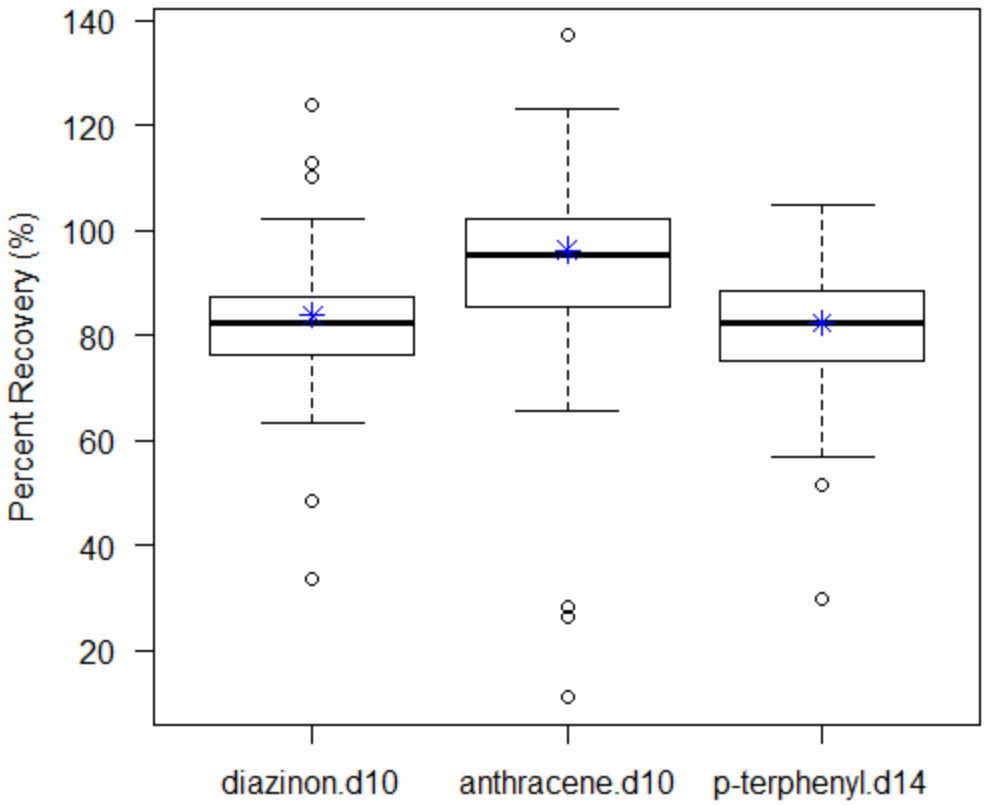

Figure S1. Distributions of percent recoveries (%) of surrogate standards in dust samples.

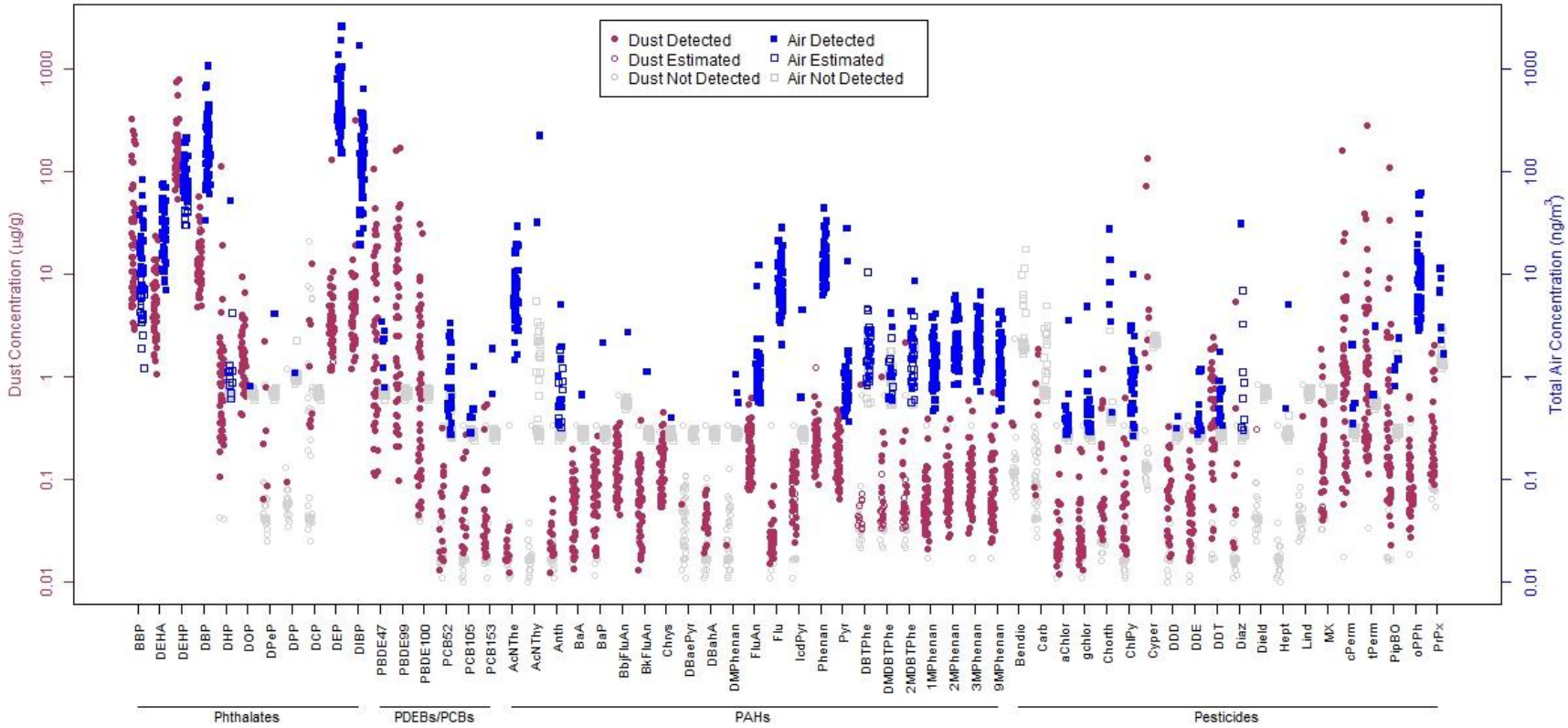

Figure S2. SVOC concentrations in house dust (left; maroon) and indoor air (right; blue) for 60 chemicals detected in either dust or air. Total air concentration comprises gas-phase and particle-phase air concentrations. Detects are values above the MRL, estimated values fall below the MRL but reported by the laboratory, and nondetects represent sample size-adjusted MRLs. Abbreviations are matched to full names in Table S1. Note log-scales.

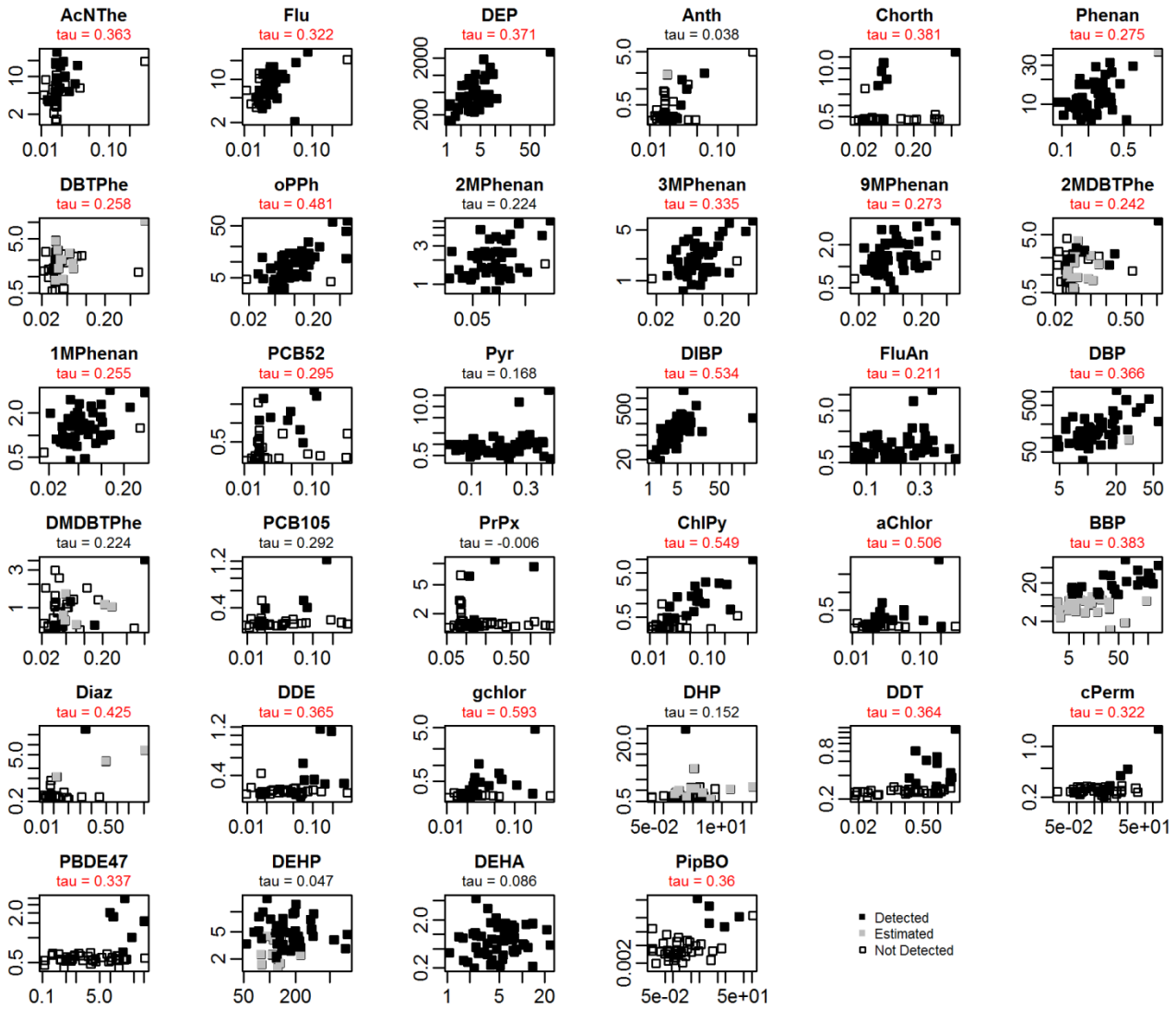

Figure S3. Measured gas-phase+particle-phase air concentrations (y-axis; ng/m^3) versus measured dust concentration (x-axis; µg/g) for 34 chemicals with at least 3 detects in air and dust. Kendall's tau correlation coefficients shown above graph: red indicates significant correlation ($p<0.05$); whereas, gray text indicates non-significance. Compounds sorted by log K_{oa}.

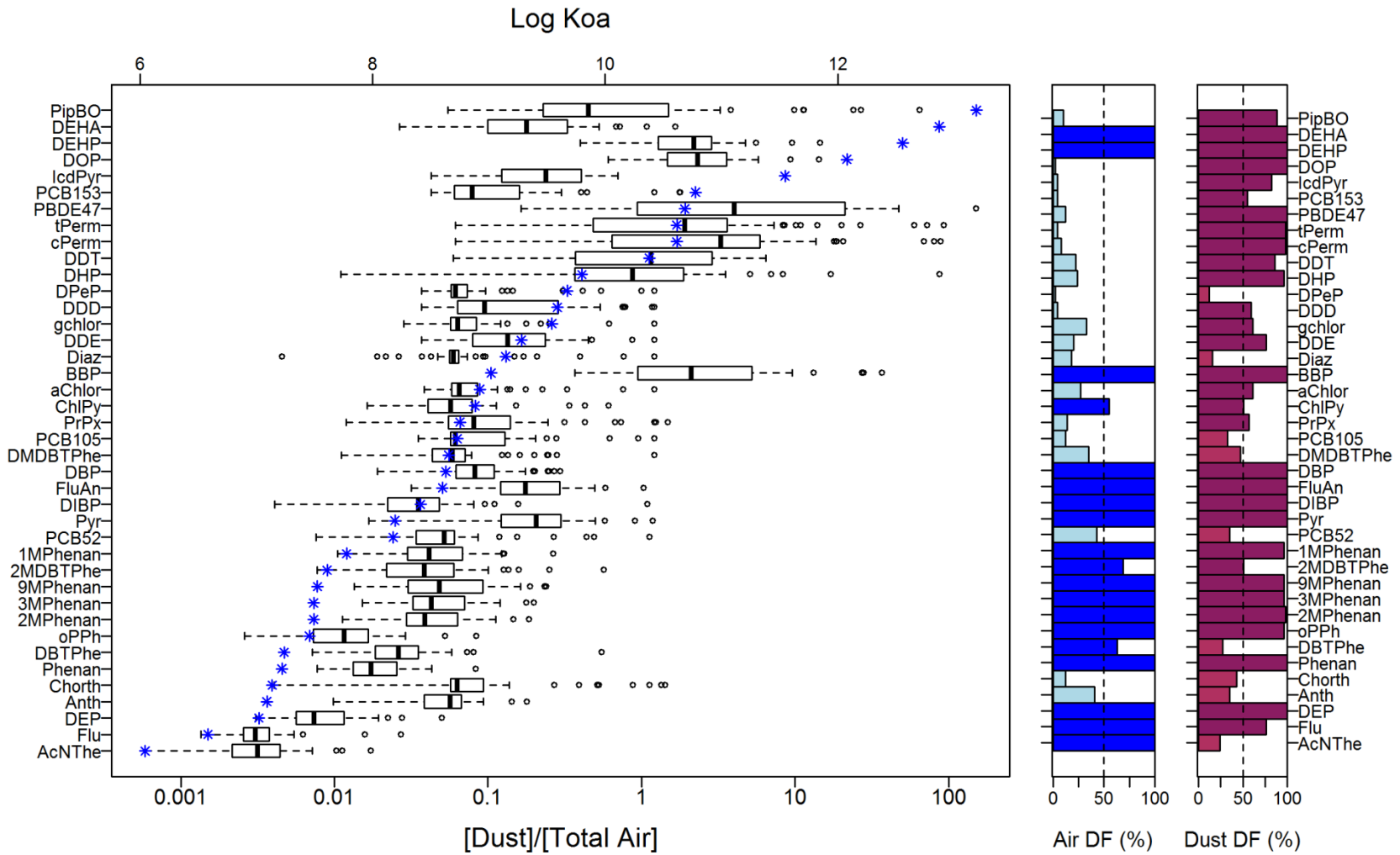

Figure S4. Ratio of measured dust concentration to gas-phase+particle-phase (total) air concentrations for 40 chemicals simultaneously detected in dust and air. Ratios are sorted by estimated log K_{oa} values (indicated by *). Nondetects have been replaced with method reporting limit. Detection frequency (% above MRL) for air and dust presented in same order.

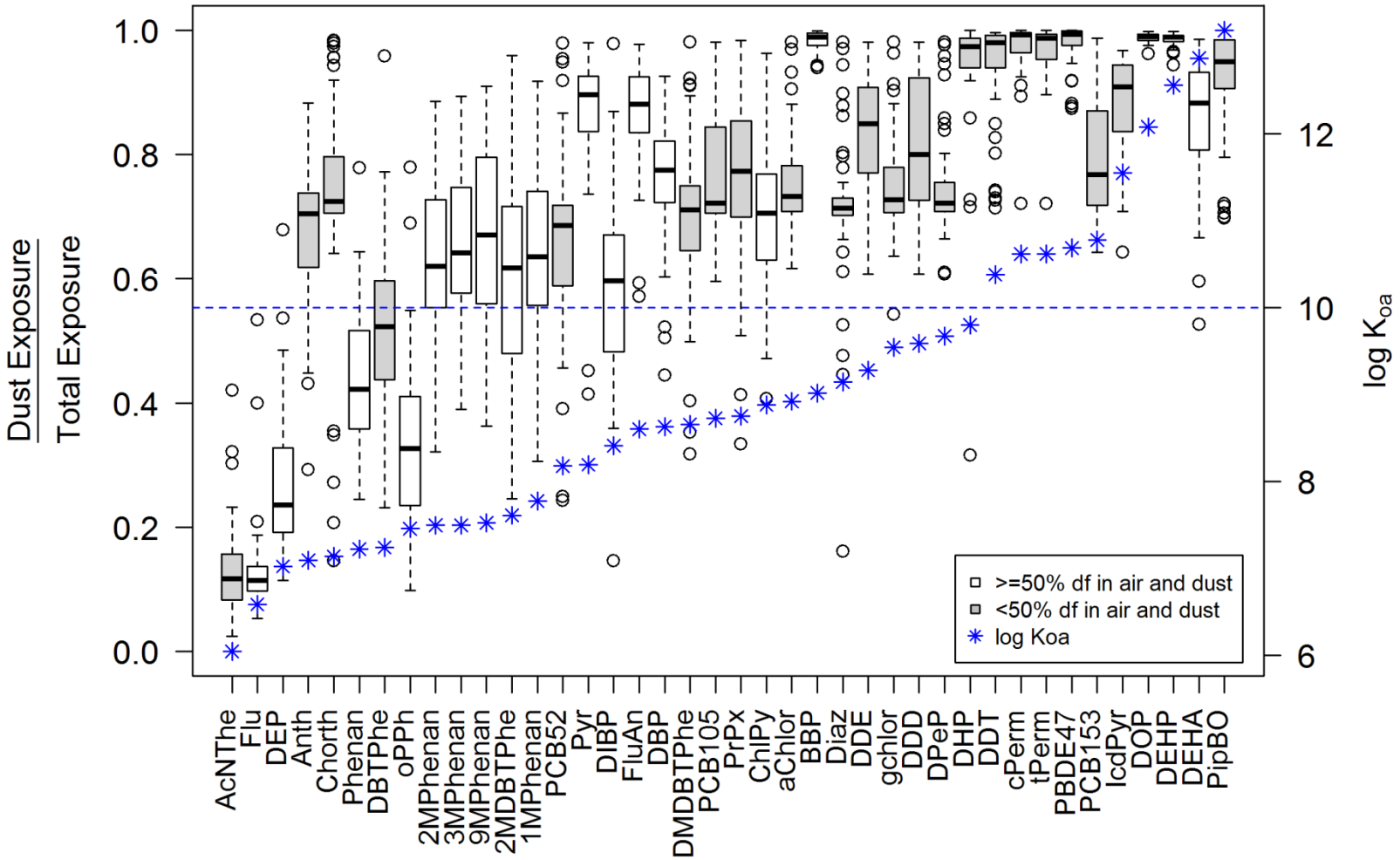

Figure S5. Relative contribution of dust exposures (ingestion and dermal) to total residential exposures (dust ingestion, dermal exposure to dust, and air inhalation) for 40 chemicals simultaneously detected in dust and air. Ratios are sorted by estimated log K_{oa} values. Dashed blue line at log K_{oa} equals 10.

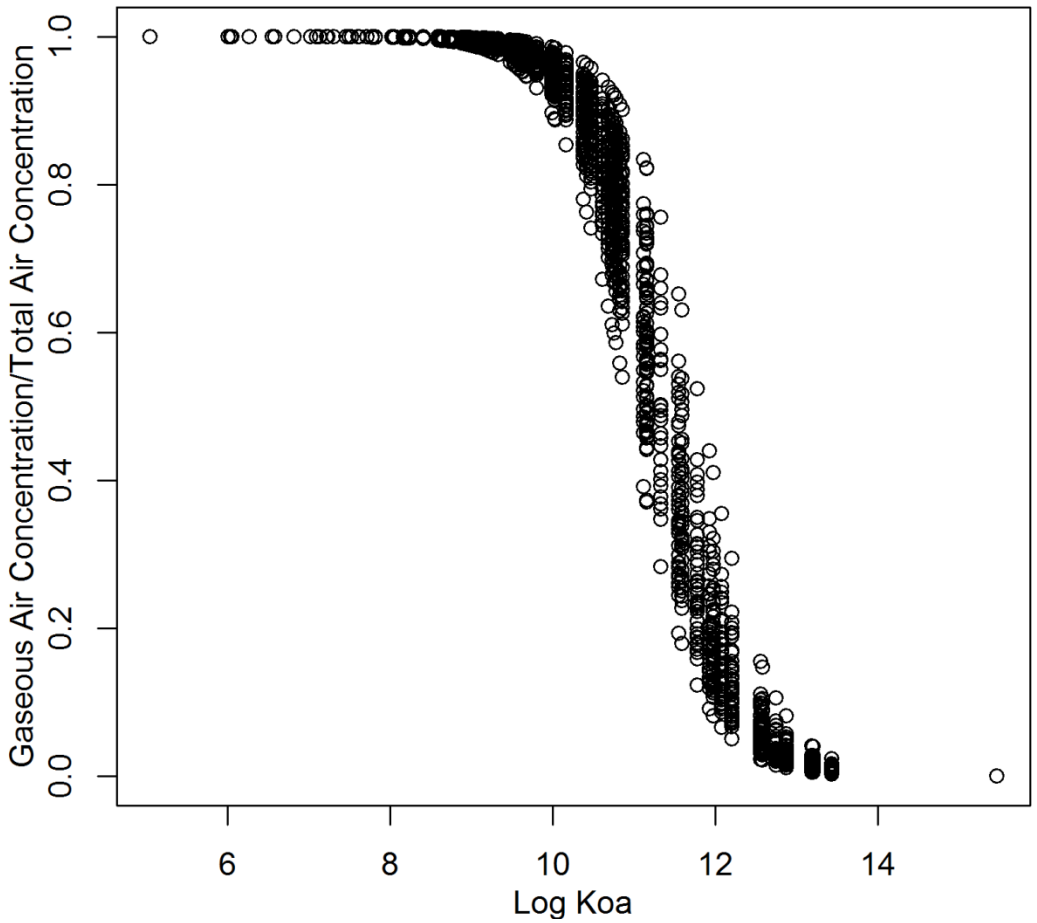

Figure S6. Ratio of estimated gas-phase air concentration to total measured air concentration for 103 chemicals detected in indoor air with available log K_{oa} values. Ratios sorted by log K_{oa} values. Note air concentrations comprise mostly gas-phase concentrations up to approximately log K_{oa} of 10. Variability driven mostly by variability in measured $PM_{2.5}$ concentrations. Points are overlayed and extreme points (highest and lowest log K_{oa}) may represent many households.

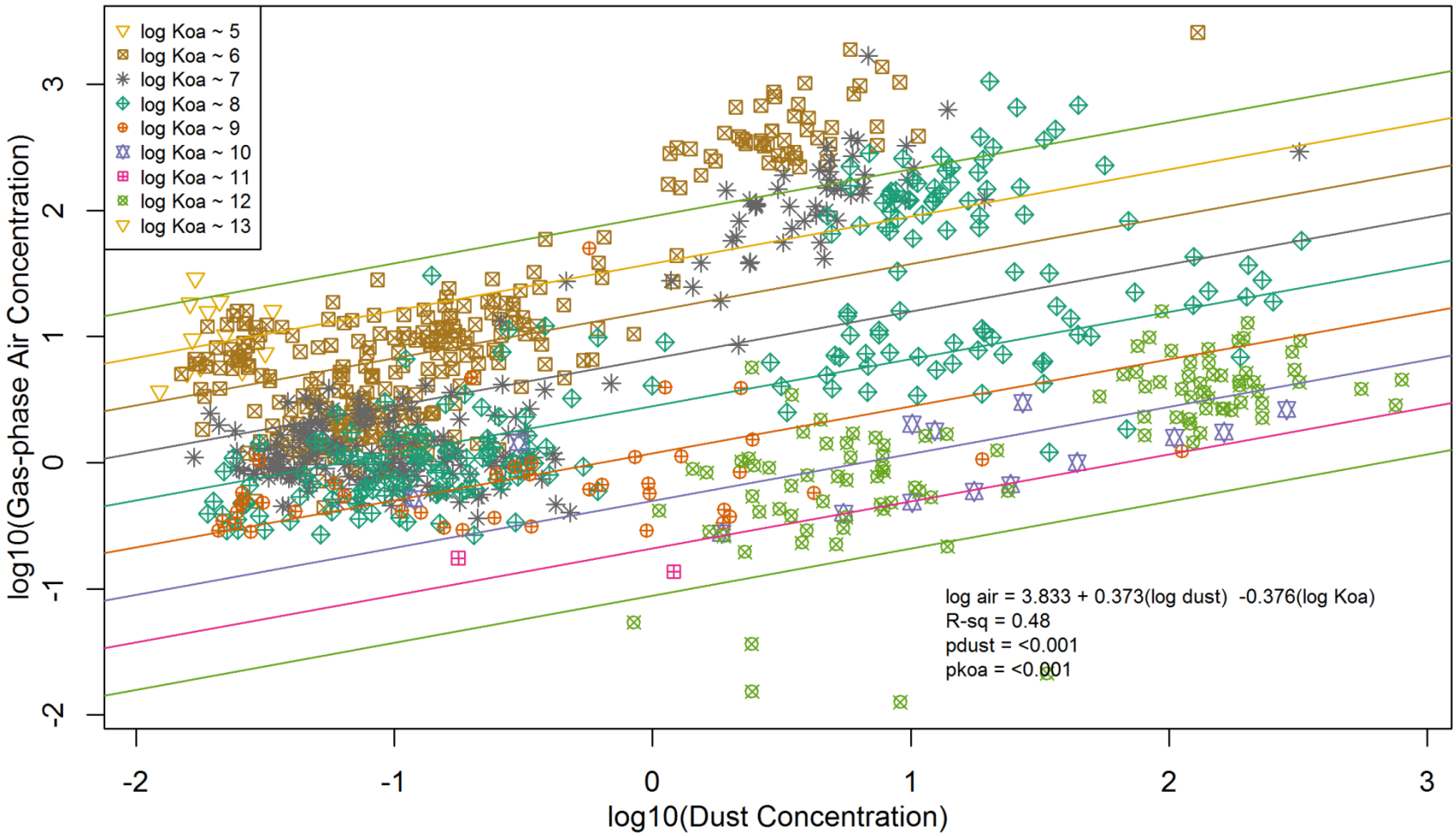

Figure S7. Log 10-based estimated gas-phase air concentration versus log 10-based measured dust concentration for 40 simultaneously detected chemicals. Symbols and colors indicate rounded chemical-specific estimated log K_{oa} values. Mixed-effects model presented; both measured dust and log Koa values are significant predictors of gas-phase air concentration ($p<0.05$). Colored lines represent regression lines for each rounded log K_{oa} value.

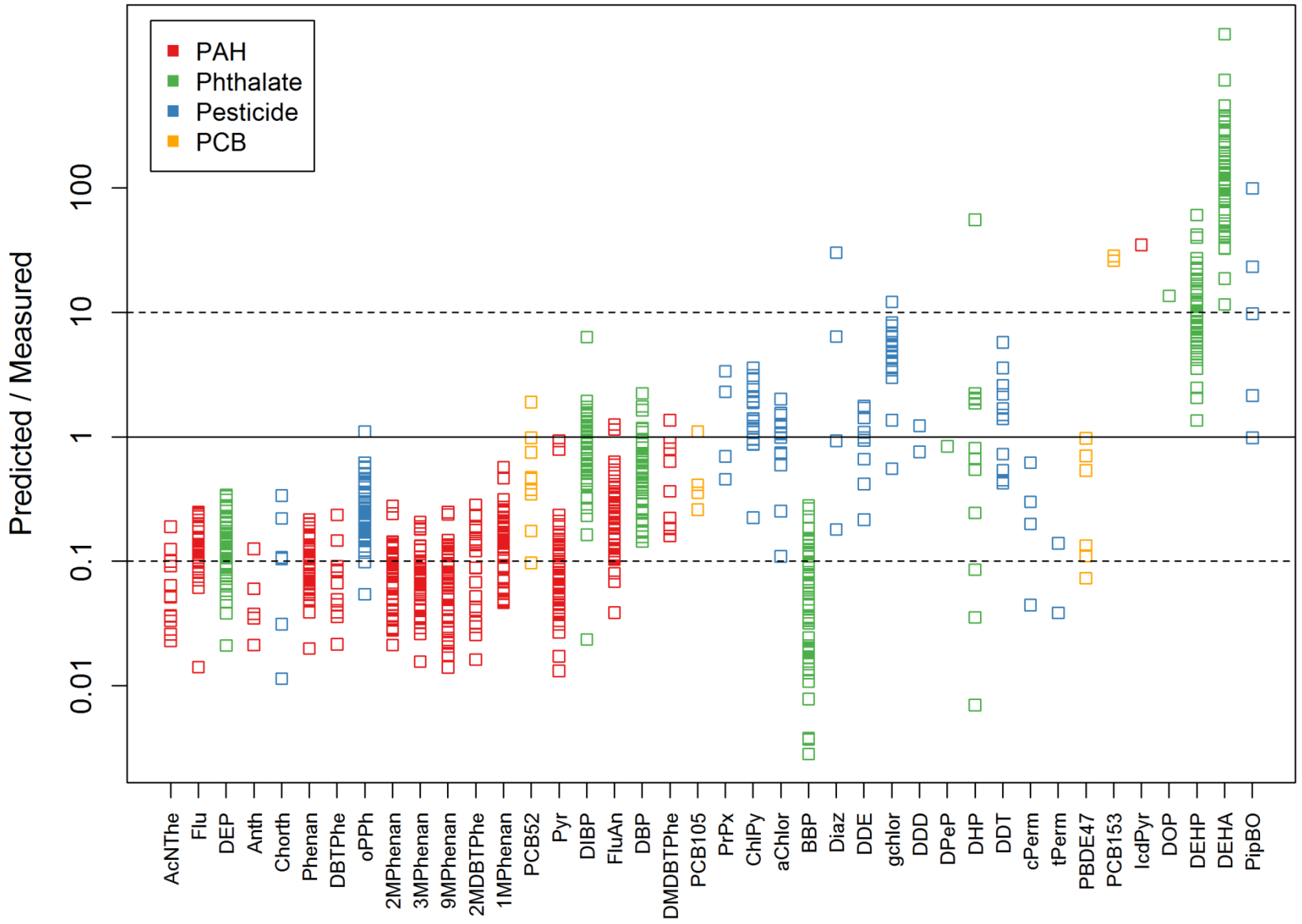

Figure S8. Ratios of predicted to measured dust concentration for 40 chemicals simultaneously detected in dust and air.

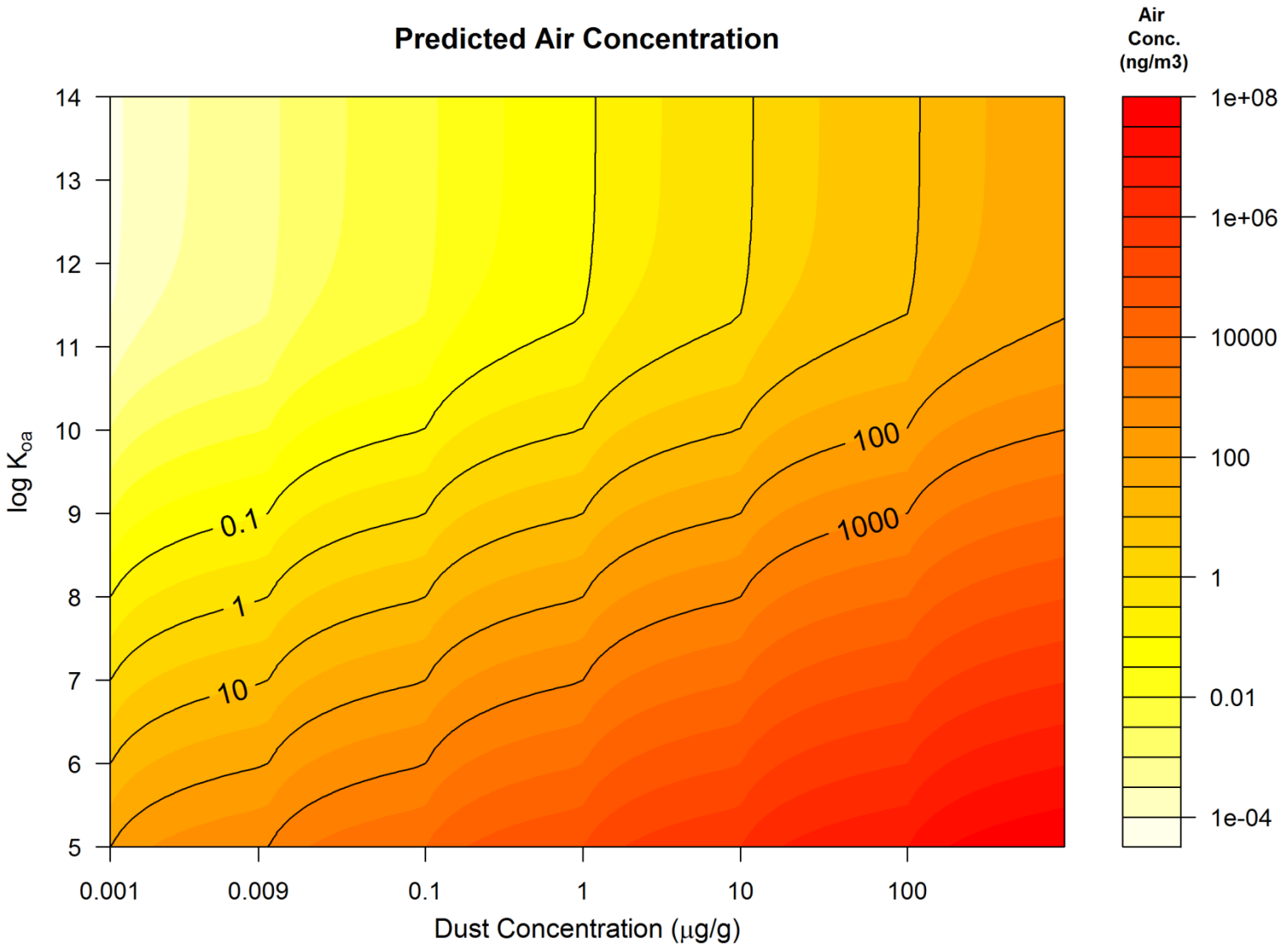

Figure S9. Contour plot of predicted air concentrations based on theoretical partitioning model using dust concentration and log K_{oa}. For example, lower molecular weight phthalates (e.g. DEP) are typically detected in dust at central tendency concentrations ranging from 10 to 100 μg/g and have log K_{oa} values of 7 to 9. Predicted air concentrations would range from 100 to >10,000 ng/m^3.